NEW INSIGHT INTO SUPRAMOLECULAR STRUCTURE FORMATION OF POLYHEDRAL OLIGOMERIC SILSEQUIOXANE (POSS) BASED ABₙ TYPE GIANT SHAPE AMPHIPHILES: LINKER’S EFFECTS

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Ruimeng Zhang

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NEW INSIGHT INTO SUPRAMOLECULAR STRUCTURE FORMATION OF POLYHEDRAL OLIGOMERIC SILSEQUIOXANE (POSS) BASED AB\textsubscript{n} TYPE GIANT SHAPE AMPHIPHILES: LINKER’S EFFECTS

Ruimeng Zhang

Thesis

Approved:  
Advisor  
Dr. Stephen Z.D. Cheng

Accepted:  
Dean of the College  
Dr. Eric J. Amis

Faculty Reader  
Dr. Toshikazu Miyoshi

Dean of the Graduate School  
Dr. Chand Midha

Department Chair  
Dr. Coleen Pugh

Date
ABSTRACT

Giant molecules have become a hot research topic in recent years. Among the family of giant molecules, a novel set of ABₙ type giant shape amphiphiles, which are constructed by one hydrophilic POSS cage with several hydrophobic POSS cages have been demonstrated to be an ideal platform to achieve various supramolecular structures. Besides the common structures (such as double gyroid (DG), hexagonally packed cylinders (HEX), body center cubic (BCC) etc.), several Frank-Kasper phases (A15, Sigma phase) as well as 12-fold quasi crystal phase can also be observed by varying the number of hydrophobic POSS cage. Obviously, there are two major factors in this system, one is the number of POSS cage (n), another one is the linker between them. Herein, we focused on the study of effects by linkers on the final supramolecular structure formation. To study this, a series of POSS based ABₙ type giant molecules with similar topological structures but different chain length was synthesized via several efficient chemistry methods. With the change of chain length, several obvious changes in supramolecular structure formation have been observed (such as from amorphous to A15 phase, A15 phase to HEX, HEX to DG etc.). This study would provide a new insight into the supramolecular structure formation of ABₙ type soft materials.
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CHAPTER I
INTRODUCTION

In recent years, a novel system called giant molecules, which refers to precisely defined macromolecules, was proposed in our group. And the diverse self-assembly behaviors of these giant molecules have attracted more and more research interests. In order to construct these giant molecules, molecular nanoparticles (MNP), such as polyhedral oligomeric silsesquioxane (POSS), polyoxometalates (POMs), fullerences, and folded globular proteins etc. with precisely defined chemical structures as well as versatile functionalities were brought into the system. In the meanwhile, the utilization of efficient chemistry, for example copper-catalyzed azide–alkyne cycloaddition (CuAAC), thio–ene “click” chemistry and atom transfer radical polymerization (ATRP) etc., also ensured the precision of target giant molecules.

The resulting giant molecules include but not only giant surfactants, giant polyhedra and giant shape amphiphiles. Giant surfactants, compared with small molecule surfactants, keep the major surfactants’ structure features but with increasing size of several nanometers. The most intriguing phenomenon observed by Xinfei and coworkers was that their self-assemble behaviors showed a duality of block copolymers and small-molecule surfactants and giant surfactants have filled the gap between them. Giant polyhedra are formed by placing MNP in the apexes of a polyhedron. Soft or rigid giant polyhedra caused by different linkers might have different self-assembly behaviors.
Shape amphiphiles were defined as molecular segments.\textsuperscript{14} Their distinct 3D shapes as well as competing interactions may afford additional parameters for self-assembled structures.\textsuperscript{15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{giant_molecules.png}
\caption{Overview of Giant Molecules}
\end{figure}

Shape amphiphiles as well as amphiphilic giant polyhedra all have Janus features.\textsuperscript{16} Molecules with two sides or at least two different chemistry or polarity were firstly named Janus particles by De Gennes by analogy to an ancient Roman double-faced god Janus.\textsuperscript{17} In the last few years, Janus particles have roused widely interest since its dissymmetry features might lead to various novel properties and interesting assembled structures.\textsuperscript{18} Based on different architecture and dimensionality, Janus particles can be generally divided into some major classes including Spherical (3D), two kinds of disc-like (2D) and two kinds of cylindrical (1D) Janus particles.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{janus_particles.png}
\caption{Overview of Janus Particles}
\end{figure}
In synthesis, the first step to create Janus feature is breaking symmetry. Although the synthetic approach\textsuperscript{20} to Janus particles had major developments in the last few years, the precise synthesis of Janus particles with high uniformity, which has significant influence on the formation of 3D long-range order, was still a great challenge.\textsuperscript{19} Janus entities provide an alternative, for example, Perce, V. et al. developed “Janus dendrimers”\textsuperscript{21} with various morphologies in water, however due to the flexible conformations, Janus entities are usually lack of shape persistent. Yiwen Li and coworkers\textsuperscript{22} firstly reported an approach (Figure 1.1) to synthesizing giant shape amphiphiles with Janus properties based on POSS(s) cage whose diameter is about 1.0 nm.\textsuperscript{23} Rigid conformation and versatile functionalities of POSS(s) cage opened up the access to Janus particles with shape persistent and precision molecular structure. The study of their self-assemble showed that AB type POSS based Janus particles with one hydrophilic POSS as one side and one hydrophobic POSS as another side could form a layered structure. One step further, if we increase one side of the Janus particle and change the AB type into AB\textsubscript{n} type, what would be the difference of their self-assembly behaviors?

![Figure 1.3 Synthetic Scheme for BPOSS-XPOSS Janus Particles](image)

(i) Phthalic anhydride, DMAP, triethylamine, THF, rt, 90%; (ii) PSS-(3-hydroxyethyl)-heptavinyl substituted (VPOSS-OH), DMAP, DIPC dry CH\textsubscript{2}Cl\textsubscript{2}, 0 °C, 93%; (iii) R\textsubscript{2}SH, DMPA, THF, rt, 15min, 77-83%.
In fact, our other study has demonstrate that when we transform the AB type giant molecule into AB\textsubscript{n} type, besides the common structures (DG, HEX, BCC etc.), several Frank-Kasper phases (A15, Sigma phase) as well as 12-fold quasi crystal phase can also be observed by varying the number of hydrophobic POSS cage.\textsuperscript{24}

Frank-Kasper phases are defined as tetrahedrally packed structures with inequivalent sites.\textsuperscript{25} Up to now, Frank-Kasper phases, including A15, sigma phase, have been observed in dendron system\textsuperscript{24}, diblock copolymer system\textsuperscript{26} as well as giant polyhedra system etc. in soft material systems. And their basic building blocks are all conical shape molecules. Thus it would be of great interest to study the self-assembled behaviors of AB\textsubscript{n} type of Janus particles.

Obviously, besides the number of POSS cage, the linker between hydrophilic and hydrophobic POSS cages is an another major factor of the formation of supramolecular structures. Herein, we reported an efficient synthetic route towards a novel a series of POSS based AB\textsubscript{n} type giant molecules with similar topological structures but different chain length. The study of their self-assembly behaviors provide a new insight into the supramolecular structure formation of AB\textsubscript{n} type soft materials.

In Chapter II, the synthetic route of AB\textsubscript{n} type giant shape amphiphiles with similar topological structures but different chain length was presented. The utilization of copper-catalyzed azide–alkyne cycloaddition (CuAAC), thio-ene “click” chemistry ensured the precision of the target giant molecules. \textsuperscript{1}H Nuclear Magnetic Resonance (NMR), \textsuperscript{13}C NMR spectra and Matrix-assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) spectra were efficient ways to prove the successful synthesis of the resulting molecules.
In Chapter III, the self-assembly behaviors of resulting molecules were observed. The ABn type giant shape amphiphiles were annealed in different temperature. Small Angle X-ray Scattering (SAXS) was applied to analyze the promising self-assembly behaviors.
CHAPTER II
SYNTHESIS OF ABₙ TYPE GIANT SHAPE AMPHIPHILES WITH SIMILAR TOPOLOGICAL STRUCTURES BUT DIFFERENT CHAIN LENGTH

2.1 Chemical and Solvent

Dichloromethane (DCM, Sigma-Aldrich, >99%), Hexanes (Sigma-Aldrich, >98%), tetrahydrofuran (THF, Sigma-Aldrich, >99%), ethyl acetate (EA, Certified ACS), ethanol (Certified ACS), methanol (MeOH, Certified ACS), cuprous bromide (CuBr, Aldrich, 98%), N,N,N′,N′′,N′′'-pentamethyldiethylenetriamine (PMDETA, Sigma-Aldrich, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, CHEM-IMPEX INT’L INC, 99%), N, N′-diisopropylcarbodiimide (DIPC, CHEM-IMPEX INT’L INC, 99%), Succinic Anhydride (Sigma-Aldrich, >99%), 10-Undecyn-1-ol (Sigma-Aldrich, >95%), 4-pentynoic acid (Sigma-Aldrich, 95%), Propiolic acid (Sigma-Aldrich, 95%), 1,1,1-Tris(hydroxymethyl)ethane (Sigma-Aldrich, 99%), 2,2-dimethoxypropane (Alfa Aesar, 98%), 2,2-bis (hydroxymethyl) propionic acid (TCL, >97%), amberlyst® 15 (H) (Acros organic), 2-methyl-2-propanethiol (Sigama-Aldrich, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Sigama-Aldrich, 99%), triethylamine (N(Et)₃, Aldrich, >99%), sodium sulfate anhydrous (Sigama-Aldrich, >99%), sulfuric acid (Sigama-Aldrich, 95%). Propargyl alcohol (Sigama-Aldrich, 99%) was used after distillation. VPOSS-OH, VPOSS-OH-S, VPOSS-COOH, BPOSS-OH, BPOSS-COOH, 3N₃-OH, N₃-3OH and N₃-Ph-COOH were successfully synthesized as previous reported methods.
2.2 Characterization

Samples were dissolved into CDCl$_3$ (Aldrich, 99.8 % D) to acquire all $^1$H and $^{13}$C NMR spectra by Varian Mercury 300 NMR spectrometer. The $\delta$ 7.27 ppm peak of $^1$H NMR spectra and the $\delta$ 77.00 ppm peak of $^{13}$C NMR spectra was the reference peak from CDCl$_3$.

MALDI-MS experiments were conducted on a Bruker UltraFlex-III TOF/TOF mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a Nd:YAG laser (355 nm). The matrix was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, > 98 %). The cationization salts were Sodium trifluoroacetate (Aldrich, >99%). All matrix (20 mg/ml) and cationization (10 mg/ml) agent and samples (10 mg/mL) were prepared in THF. Then mixed those solutions in the ratio of matrix/sample/cationizing agent = 10:2:1. 0.5–1.0 µL of the final mixed solution was deposited into the MALDI sample plate. The solvent was allowed to evaporate at rt. This procedure made the formation of [M·Na]$^+$ ions. Positive linear mode was applied to all spectra.

Silica gel plates were used to analyze the products in each synthetic step. The samples were spotted on the silica gel plates and developed using different mixture of solvents, such as DCM, hexane, EA and ethanol.

2.3 Synthetic Procedures

The products in each synthetic step were successfully synthesized via following methods. $^1$H NMR, $^{13}$C NMR, and MALDI-TOF mass spectra can proved the precise synthesis of the final resulting molecules.
2.3.1 Synthesis of 2,2,5-Trimethyl-1,3-dioxane-5-carboxylic Anhydride (TMDOCA)

The 2,2-bis (hydroxymethyl) propionic acid (10g, 74.55mmol), 2,2-dimethoxypropane (11.6g, 111.38mmol), were dissolved by 25ml acetone, followed by adding amberlyst® 15 (H) (100mg). The mixture was capped and stirred for 2h. After that, the precipitates were filtered off. After solvent removal, the residual was added in to another 500ml round-bottomed flask, followed by adding dried DCM (60ml). The mixture was cooled to 0 °C, then DIPC (9.37g, 74.25mmol) was added. After that, the mixture was stirred for 10h under room temperature (rt). Then the white precipitates were filtered off. After solvent removal, the residual was dissolved into EA and the precipitates were filtered off. The last step was repeated for 3 times to remove the excess DIPC. The TMDOCA(8.10g, 66%) as faint yellow viscous liquid was protected from light in a dry place. $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 4.23-3.66 (dd, 8H, -C$_2$H$_2$O-), 1.44-1.40 (d, 12H, -O$_2$C(CH$_3$)$_2$), 1.24 (s, 6H, -C(CH$_2$)$_2$CH$_3$).

2.3.2 Synthesis of VPOSS-diOH-1

The VPOSS-OH (500 mg, 0.77 mmol), DMAP (93.86 mg, 0.77 mmol) and N(Et)$_3$ (77.72 mg, 0.77 mmol) were totally dissolved by 15 ml dry THF. The mixture was cooled to 0 °C, then, TMDOCA (2.03 g, 6.16 mmol) was added. After that, the mixture was stirred under rt for 24h. To quench the reaction, 5 ml water was added and stirred for 1h. After that, the solution was concentrated to ~5ml, washed with saturated sodium bisulfate solution (125 ml deionized water, 7 g sodium sulfate anhydrous and 5 g sulfuric acid) and extracted with DCM. After solvent removal, silica gel column chromatography using DCM as the eluent was applied to purify the residue and acquire the precursor as a colorless gel.
Then the precursor was fully dissolved into MeOH/THF=1/1, followed by adding amberlyst® 15 (H) (100 mg). The mixture was stirred for 48h. After solvent removal, silica gel column chromatography using DCM/EtOH=20/1 as the eluent was applied to purify the residue and acquire the product as a white powder (480 mg, 75.35%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 6.16-5.86 (m, 21H, -CH=CH$_2$), 4.32 (t, 2H, -SCH$_2$CH$_2$O-), 3.88-3.70 (dd, 4H, -CH$_2$OH), 2.81 (t, 2H, -SCH$_2$CH$_2$O-), 2.69 (t, 2H, -SiCH$_2$CH$_2$S-), 1.10 (s, 3H, -C(CH$_2$)$_2$CH$_3$-), 1.07 (t, 2H, -SiCH$_2$CH$_2$S-).

Figure 2.1 Synthetic Route for VPOSS-diOH-1

2.3.3 Synthesis of VPOSS-diyne-1

The VPOSS-diOH-1 (250 mg, 0.30 mmol), 4-pentyonic acid (89.27 mg, 0.91 mmol), DMAP (73.302 mg, 0.60 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (75.72 mg, 0.60 mmol) dropwise. After that the mixture was stirred under rt for 24h. After solvent removal, silica gel column chromatography using DCM as the eluent was applied to purify the residue and acquire the product as a white powder (236 mg, 80%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 6.15-5.84 (m, 21H, -CH=CH$_2$), 4.28-4.26 (d, 4H, -C(CH$_3$)CH$_2$O-), 4.25 (t, 2H, -SCH$_2$CH$_2$O-), 2.74 (t, 2H, -SCH$_2$CH$_2$O-), 2.66 (t, 2H, -SiCH$_2$CH$_2$S-), 2.58-2.44 (m, 8H, -CH$_2$CH$_2$C≡CH), 1.97 (t, 2H, -CH$_2$CH$_2$C≡CH), 1.26 (s, -C(CH$_3$)CH$_2$O-), 1.06 (t, 2H, -SiCH$_2$CH$_2$S-).
2.3.4 Synthesis of VPOSS-dioH-2

The VPOSS-COOH (1000 mg, 1.38 mmol), 1,1,1-Tris (hydroxymethyl)ethane (496.22 mg, 4.13 mmol), DMAP (168.64 mg, 1.38 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (174.16 mg, 1.38 mmol) dropwise. After that the mixture was stirred under rt for 24h. After solvent removal, silica gel column chromatography using DCM/EA=10/1 as the eluent was applied to purify the residue and acquire the product as a white powder (810 mg, 71%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 6.15-5.85 (m, 21H, -CH=CH$_2$), 4.22 (s, 2H, -CH$_3$O-), 3.57-3.56 (d, 4H, -CH$_2$OH), 3.27 (s, 2H, -SCH$_2$CO-), 2.77 (t, 2H, -SiCH$_2$CH$_2$S-), 2.68 (t, 2H, -CH$_2$OH), 1.09 (t, 2H, -SiCH$_2$CH$_2$S-), 0.85 (s, 3H, - CH$_3$).
2.3.5 Synthesis of VPOSS-diyne-2

The VPOSS-diOH-2 (500 mg, 0.61 mmol), 4-pentynoic acid (237.402 mg, 2.42 mmol), DMAP (149.084 mg, 1.22 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (305.40 mg, 2.42 mmol) dropwise. After that the mixture was stirred under rt for 24h. After solvent removal, silica gel column chromatography using DCM as the eluent was applied to purify the residue and acquire the product as a white powder (236 mg, 80%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 6.16-5.85 (m, 21H, -CH=CH$_2$), 4.08 (s, 2H, -CH$_2$O-), 4.06 (s, 4H, -CH$_3$O-), 3.24 (s, 2H,-SCH$_2$CO-), 2.76 (t, 2H, -SiCH$_2$CH$_3$S-), 2.63-2.47 (m, 8H, -CH$_2$CH$_2$C≡CH), 2.00 (t, 2H, -CH$_2$CH$_2$C≡CH), 1.09 (t, 2H, -SiCH$_2$CH$_2$S-), 1.05 (s, 3H, -CH$_3$).

![Figure 2.4 Synthetic Route for VPOSS-diyne-2](image)

2.3.6 Synthesis of BPOSS-COOH-L

The BPOSS-OH (1000.00mg, 1.08mmol), DMAP (395.93mg, 3.24mmol), succinic anhydride (324.06mg, 3.24mmol) were totally dissolved by dry THF. The mixture was cooled to 0 °C, then N(Et)$_3$ (327.86mg, 3.24mmol) was added. After that the mixture was stirred under rt for 24h. To quench the reaction, 5 ml water was added and stirred for 1h. After that, the solution was concentrated to ~5ml, washed with saturated sodium bisulfate solution (125ml deionized water, 7 g sodium sulfate anhydrous and 5g sulfuric acid) and extracted with DCM. After solvent removal, silica gel column chromatography using
DCM/EA=10/1 as the eluent was applied to purify the residue and acquire the product as white power (937mg, 85%). $^1\text{H}$ NMR (300 MHz, CDCl$_3$, ppm, $\delta$): 4.24 (t, 2H, -SCH$_2$CH$_2$O-), 2.75 (t, 2H, -SCH$_2$CH$_2$O-), 2.71-2.61 (m, 6H, -COCH$_2$CH$_2$COOH, -SiCH$_2$CH$_2$S-), 1.85 (m, 7H, -SiCH$_2$CH(CH$_3$)$_2$), 0.97-0.94 (dd, 42H, -SiCH$_2$CH(CH$_3$)$_2$), 0.61 (t, 2H, -SiCH$_2$CH$_2$S-), 0.60 (t, 14H, -SiCH$_2$CH(CH$_3$)$_2$).

**Figure 2.5 Synthetic Route for BPOSS-COOH-L**

(i) Succinic anhydride, DMAP, N(Et)$_3$, dry THF, rt, 24h, 85%-90%.

2.3.7 Synthesis of BPOSS-N$_3$-S

The BPOSS-OH (500 mg, 0.54 mmol), N3-Ph-COOH (191.33 mg, 1.08 mmol), DMAP (65.99 mg, 0.54 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (68.15 mg, 0.54 mmol) dropwise. After that, the mixture was stirred under rt for 24h. After solvent removal, silica gel column chromatography using DCM/Hexane=2:1 as the eluent was applied to purify the residue and acquire the product as a white powder (156.78mg, 520mg 89%). $^1\text{H}$ NMR (300 MHz, CDCl$_3$, ppm, $\delta$): 8.04-7.37 (4H, dd, aromatics), 4.61(s, 2H, -CH$_2$N$_3$), 4.41 (s, 2H, -CH$_2$OCOPh-), 2.74 (t, 2H, -SCH$_2$CH$_2$O-), 2.64 (m, 2H, -SiCH$_2$CH$_2$S-), 1.85 (m, 21H, -SiCH$_2$CH(CH$_3$)$_2$), 0.97-0.94 (dd, 42H, -SiCH$_2$CH(CH$_3$)$_2$), 0.61 (t, 2H, -SiCH$_2$CH$_2$S-), 0.60 (t, 14H, -SiCH$_2$CH(CH$_3$)$_2$).
2.3.8 Synthesis of VPOSS-yne-S

The VPOSS-OH-S (500 mg, 0.77 mmol), propiolic acid (107.88 mg, 1.54 mmol), DMAP (94.10 mg, 0.77 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (194.35 mg, 1.54 mmol) dropwise. After that the mixture was stirred under rt for 24h. After solvent removal, silica gel column chromatography using DCM/Hexane=1:1 as the eluent was applied to purify the residue and acquire the product as a white powder (334.28 mg, 63 %). $^1$H NMR (300 MHz, CDCl$_3$, ppm, $\delta$): 6.16-5.86 (m, 21H, -CH=CH$_2$), 4.26 (t, 2H, -SiCH$_2$CH$_2$O-), 1.97 (s, 1H, -C≡CH), 1.22 (t, 2H, -SiCH$_2$CH$_2$O-).

(i) Propiolic acid, DMAP, DIPC, rt, 24h, 60%-70%.

Figure 2.7 Synthetic Route for VPOSS-yne-S
2.3.9 Synthesis of VPOSS-yne-L

The VPOSS-COOH (1 g, 1.38 mmol), Propargyl alcohol(115.96 mg, 2.06 mmol), DMAP (168.59 mg, 1.38 mmol) were totally dissolved by dry THF and then cooled to 0 °C, followed by adding DIPC (348.31 g, 2.76 mmol) dropwise. After that, the mixture was stirred under rt for 24h. After solvent removal, silica gel column chromatography using DCM/Hexane=1/1 as the eluent was applied to purify the residue and acquire the product as a white powder (826.99 mg, 78.52%). \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm, δ): 6.16-5.86 (m, 21H, \(-\text{CH=CH}_2\)) , 4.74 (d, 2H, \(-\text{OCH}_2\text{C}=\text{CH}\) ), 3.28 (s, 2H, \(-\text{SCH}_2\text{CO}-\) ), 2.78 (t, 2H, \(-\text{SiCH}_2\text{CH}_2\text{S}-)\), 2.49 (t, 1H, \(-\text{OCH}_2\text{C}=\text{CH}\) ), 1.10 (t, 2H, \(-\text{SiCH}_2\text{CH}_2\text{S}-)\).

![Diagram](image)

(i) Propargyl alcohol, DMAP, DIPC, rt, 24h, 80%-90%.

Figure 2.8 Synthetic Route for VPOSS-yne-L

2.3.10 Synthesis of N\(_3\)-3BPOSS-S

The BPOSS-COOH (500 mg, 0.53 mmol), N\(_3\)-3OH (19.34 mg, 0.12 mmol), DMAP (64.77 mg, 0.53 mmol) were totally dissolved by dry THF then cooled to 0 °C, followed by adding DIPC (133.77 mg, 1.06 mmol) dropwise. After that, the mixture was stirred under rt for 36h. After solvent removal, silica gel column chromatography using DCM/Hexane=1/1 as the eluent was applied to purify the residue and acquire the product as a white powder (293 mg, 83 %). \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm, δ): 4.17 (t, 6H, -
CH$_2$O), 3.53 (s, 2H, -CH$_3$N$_3$), 3.25 (s, 6H, -SCH$_2$CO-), 2.73 (t, 6H, -SiCH$_2$CH$_2$S), 1.87 (m, 21H, -SiCH$_2$CH(CH$_3$)$_2$), 0.99-0.96 (dd, 126H, -SiCH$_2$CH(CH$_3$)$_2$), 0.63 (t, 6H, -SiCH$_2$CH$_2$S-), 0.62 (t, 42H, -SiCH$_2$CH(CH$_3$)$_2$).

![Figure 2.9 Synthetic Route for N$_3$-3BPOSS-S](image)

(i) N$_3$-3OH, DMAP, DIpc, rt, 36h, 80%-85%.

Figure 2.9 Synthetic Route for N$_3$-3BPOSS-S

2.3.11 Synthesis of N$_3$-3BPOSS-L

The BPOSS-COOH-L (500 mg, 0.49 mmol), N$_3$-3OH (16.12 mg, 0.10 mmol), DMAP (36.67 mg, 0.30 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIpc (75.72 mg, 0.60 mmol) dropwise. After that, the mixture was stirred under rt for 36h. After solvent removal, silica gel column chromatography using DCM/EA=40/1 as the eluent was applied to purify the residue and acquire the product as a white powder (252 mg, 81%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 4.22 (t, 6H, -SCH$_2$CH$_2$O-), 4.10 (s, 6H, -CH$_3$O-), 3.46 (s, 2H, -CH$_3$N$_3$), 2.74 (t, 6H, -SCH$_2$CH$_2$O-), 2.64 (m, 18H, -SiCH$_2$CH$_2$S-, -COCH$_2$CH$_2$CO-), 1.85 (m, 21H, -SiCH$_2$CH(CH$_3$)$_2$), 0.97-0.94 (dd, 126H, -SiCH$_2$CH(CH$_3$)$_2$), 0.61 (t, 6H, -SiCH$_2$CH$_2$S-), 0.60 (t, 42H, -SiCH$_2$CH(CH$_3$)$_2$).
2.3.12 Synthesis of VPOSS-3N₃

The VPOSS-COOH (150 mg, 0.21 mmol), 3N₃-OH (39.71 mg, 0.19 mmol), DMAP (46.44 mg, 0.38 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (47.96 mg, 0.38 mmol) dropwise. After that, the mixture was stirred under rt for 4h. After solvent removal, silica gel column chromatography using DCM as the eluent was applied to purify the residue and acquire the product as a white powder (97.42 mg, 50.52%). £H NMR (300 MHz, CDCl₃, ppm, δ): 6.16-5.86 (m, 21H, -CH=CH₂), 4.04 (s, 2H, -OCH₃), 3.39 (s, 6H, -CH₂N₃), 3.26 (s, 2H, -SCH₂CO-), 2.77 (t, 2H, -SiCH₂CH₂S-), 1.10 (t, 2H, -SiCH₂CH₂S-).

Figure 2.11 Synthetic Route for VPOSS-3N₃
2.3.13 Synthesis of BPOSS-yne-L

The BPOSS-COOH (500 mg, 0.53 mmol), 10-Undecyn-1-ol (178.38 mg, 1.06 mmol), DMAP (64.77 mg, 0.53 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (133.78 mg, 1.06 mmol) was added. After that, the mixture was stirred under rt for 24h. After solvent removal, silica gel column chromatography using DCM/Hexane=1/1 as the eluent was applied to purify the residue and acquire the product as a white powder (471mg, 81%).

![Synthesis Route for BPOSS-yne-L](image)

(i) 10-Undecyn-1-ol, DMAP, DIPC, dry THF, rt, 24h, 80%-85%.

Figure 2.12 Synthetic Route for BPOSS-yne-L

2.3.14 Synthesis of NPOSS-COOH

The VPOSS-COOH (2.0g, 2.76mmol), 2-methyl-2-propanethiol (3.48g, 38.59mmol) and DMPA (10mg, 81.83mmol) were totally dissolved by dry THF. The mixture was applied to 365nm UV light for 15 min. After the solvent and residual 2-methyl-2-propanethiol were blow away in a fume hood at rt, silica gel column chromatography using DCM/EA=20:1 as the eluent was applied to purify the residue and acquire the crude product as a colorless gel. Then the crude product was precipitated into cold water. After centrifugation, the sample NEWPOSS-COOH was collected and dried overnight under vacuum to afford a white powder (2.61g, 75%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 3.79
(s, 1H, -COOH), 3.21 (s, 2H, -SiCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>), 2.73 (t, 2H, -SiCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>), 2.56 (t, 14H, -SiCH<sub>2</sub>CH<sub>2</sub>SC(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 63H, -SiCH<sub>2</sub>CH<sub>2</sub>SC(CH<sub>3</sub>)<sub>3</sub>), 1.01 (t, 2H, -SiCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>), 0.93(t, 14H, -SiCH<sub>2</sub>CH<sub>2</sub>SC(CH<sub>3</sub>)<sub>3</sub>).

2.3.15 Synthesis of NPOSS-yn e-S

The NEWPOSS-COOH (1g, 0.79mmol), Propargyl alcohol (66.83mg, 1.19mmol), DMAP (96.51mg, 0.79mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (99.70g, 0.79mmol) dropwise. After that, the mixture was stirred under rt for 24 h. After solvent removal, silica gel column chromatography using DCM as the eluent was applied to purify the residue and acquire the product as a colorless gel (783.75mg, 76.53%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm, δ): 4.72 (d, 2H, -OCH=CH), 3.25 (s, 2H, -SCH=CH-), 2.76 (t, 2H, -SiCH=CH2SCH=CH), 2.61 (t, 14H, -SiCH=CH2SC(CH=CH)-), 2.52 (t, 1H, -OCH=CH), 1.31 (s, 63H, -SiCH=CH2SC(CH=CH)-), 1.12 (t, 2H, -SiCH=CH2SCH=CH-), 0.98 (t, 14H, -SiCH=CH2SC(CH=CH)-).

![Diagrams](image)

(i) Propargyl, DMAP, DIPC, dry THF, rt, 24h, 80%-85%.

Figure 2.13 Synthetic Route for NPOSS-yn e-S
2.3.16 Synthesis of NPOSS-yne-L

The NEWPOSS-COOH (500 mg, 0.40 mmol), 10-Undecyn-1-ol (100.97 mg, 0.60 mmol), DMAP (48.88 mg, 0.40 mmol) were totally dissolved by dry THF, then cooled to 0 °C, followed by adding DIPC (100.96 mg, 0.80 mmol) dropwise. After that, the mixture was stirred under rt for 24 h. After solvent removal, silica gel column chromatography using DCM as the eluent was applied to purify the residue and acquire the product as a colorless gel (456mg, 83%).

![Chemical Structure](image)

(i) 10-Undecyn-1-ol, DMAP, DIPC, dry THF, rt, 24h, 80%-85%.

Figure 2.14 Synthetic Route for NPOSS-yne-L

2.3.17 Synthesis of Yne-diOH

The propargyl alcohol (100 mg, 1.78 mmol), DMAP (217 mg, 1.78 mmol) and N(Et)$_3$ (360 mg, 3.56 mmol) were totally dissolved by dry THF. The mixture was cooled to 0 °C, then TMDOCA (4.7 g, 14.24 mmol) was added. After that, the mixture was stirred under rt for 24 h. To quench the reaction, 5ml water was added and stirred for 1h. After that, the solution was concentrated to ~5ml, washed with saturated sodium bisulfate solution (125 ml deionized water, 7 g sodium sulfate anhydrous and 5 g sulfuric acid) and extracted with DCM. After solvent removal, silica gel column chromatography using DCM/Haxane=2/1 as the eluent was applied to purify the residue and acquire the precursor.
as a colorless gel. Then the precursor was fully dissolved into MeOH/THF=1/1, followed by adding amberlyst® 15 (H) (100mg). The mixture was stirred for 48h. After solvent removal, silica gel column chromatography using DCM/EtOH=20/1 as the eluent was applied to purify the residue and acquire the product as a colorless gel (222.38 mg, 72.56%).

1H NMR (300 MHz, CDCl₃, ppm, δ): 4.69 (d, 2H, -CH₂O-), 3.84-3.64 (dd, 4H, -CH₃OH), 3.38 (s, 2H, -OH), 2.50 (t, 1H, CH-═C-), 1.07 (s, 3H, -C(CH₂OH)₂CH₃).

2.3.18 Synthesis of VPOSS-2BPOSS-20

The VPOSS-dioH-1 (82.73 mg, 0.10 mmol), BPOSS-COOH-L (306.09 mg, 0.30 mmol), DMAP (36.67 mg, 0.30 mmol) were totally dissolved by dry THF, then cooled to 0 ºC, followed by adding DIPC (75.72 mg, 0.60 mmol) dropwise. After that, the mixture was stirred under rt for 24 h. After solvent removal, silica gel column chromatography using DCM as the eluent was applied to purify the residue and acquire the product as a white powder (198 mg, 70%).

![Chemical Structure of VPOSS-2BPOSS-20](image)

Figure 2.15 Chemical Structure of VPOSS-2BPOSS-20
Figure 2.16 $^1$H NMR Spectra of VPOSS-2BPOSS-20

Figure 2.17 $^{13}$C NMR Spectra of VPOSS-2BPOSS-20
2.3.19 Synthesis of VPOSS-2BPOSS-28

The VPOSS-diyn-1 (88.87 mg, 0.09 mmol), BPOSS-N₃-S (216.16 mg, 0.2 mmol), CuBr (5mg, 0.04 mmol) were totally dissolved by dry THF into 100 mL Schlenk flask and degassed for three times. Then PMDETA (15mg, 0.09 mmol) was added. The system was degassed again and stirred for 12 h. After the reaction was completed, the solution was added into silica gel column. THF was applied to elute the crude product off. After solvent removal, silica gel column chromatography using DCM/EA= 10:1 as the eluent was applied to purify the residue and acquire the product as a white powder (260.74 mg, 92%).
Figure 2.19 Chemical Structure of VPOSS-2BPOSS-28

Figure 2.20 $^1$H NMR Spectra of VPOSS-2BPOSS-28
Figure 2.21 $^{13}$C NMR Spectra of VPOSS-2BPOSS-28

Figure 2.22 MALDI-TOF Mass Spectra of VPOSS-2BPOSS-28
2.3.20 Synthesis of VPOSS-3BPOSS-21

VPOSS-yne-S (70.31 mg, 0.1 mmol), N₃-3BPOSS-L (311.40 mg, 0.1 mmol), CuBr (5 mg, 0.04 mmol) were totally dissolved by dry THF into 100 mL Schlenk flask and degassed for three times. Then PMDETA (15 mg, 0.09 mmol) was added. The system was degassed again and stirred for 12 h. After the reaction was completed, the solution was added into silica gel column. THF was applied to elute off the crude product. After solvent removal, silica gel column chromatography using EA/Hexane=1/2 as the eluent was applied to purify the residue and acquire the product as a white powder (355 mg, 93%).

![Chemical Structure of VPOSS-3BPOSS-21](image-url)

Figure 2.23 Chemical Structure of VPOSS-3BPOSS-21
Figure 2.24 $^1$H NMR Spectra of VPOSS-3BPOSS-21

Figure 2.25 $^{13}$C NMR Spectra of VPOSS-3BPOSS-21
2.3.21 Synthesis of VPOSS-3BPOSS-27

The BPOSS-yne-L (109.59 mg, 0.1 mmol), fresh prepared VPOSS-3N₃ (27.55 mg, 0.03 mmol), CuBr (5mg, 0.04 mmol) were totally dissolved by dry THF into 100 mL Schlenk flask and degassed for three times. Then PMDETA (15mg, 0.09 mmol) was added. The system was degassed again and stirred for 12 h. After the reaction was completed, the solution was added into silica gel column. THF was applied to elute off the crude product. After solvent removal, silica gel column chromatography using DCM/EA= 15:1 as the eluent was applied to purify the residue and acquire the product as a white powder (116 mg, 92%).

Figure 2.26 MALDI-TOF Mass Spectra of VPOSS-3BPOSS-21
Figure 2.27 Chemical Structure of VPOSS-3BPOSS-27

Figure 2.28 $^1$H NMR Spectra of VPOSS-3BPOSS-27
Figure 2.29 $^{13}$C NMR Spectra of VPOSS-3BPOSS-27

Figure 2.30 MALDI-TOF Mass Spectra of VPOSS-3BPOSS-27
2.3.22 Synthesis of VPOSS-3NPOSS-19

The NPOSS-yne-S (380.44 mg, 0.29 mmol), fresh prepared VPOSS-3N₃ (77 mg, 0.08 mmol), CuBr (5 mg, 0.04 mmol) were totally dissolved by dry THF into 100 mL Schlenk flask and degassed for three times. Then PMDETA (15 mg, 0.09 mmol) was added. The system was degassed again and stirred for 12 h. After the reaction was completed, the solution was added into silica gel column. THF was applied to elute off the crude product. After solvent removal, silica gel column chromatography using DCM/EA= 15:1 as the eluent was applied to purify the residue and acquire the product as a colorless gel (330.98 mg, 81.22%).

Figure 2.31 Chemical Structure of VPOSS-3NPOSS-19
Figure 2.32 $^1$H NMR Spectra of VPOSS-3NPOSS-19

Figure 2.33 $^{13}$C NMR Spectra of VPOSS-3NPOSS-19
2.3.23 Synthesis of VPOSS-3NPOSS-27

The NPOSS-yne-L (140.86 mg, 0.1 mmol), fresh prepared VPOSS-3N₃ (27.55 mg, 0.03 mmol), CuBr (5mg, 0.04 mmol) were totally dissolved by dry THF into 100 mL Schlenk flask and degassed for three times. Then PMDETA (15mg, 0.09 mmol) was added. The system was degassed again and stirred for 12 h. After the reaction was completed, the solution was added into silica gel column. THF was applied to elute off the crude product. After solvent removal, silica gel column chromatography using DCM/EA= 10:1 as the eluent was applied to purify the residue and acquire the product as a colorless gel (140 mg, 91%).
Figure 2.35 Chemical Structure of VPOSS-3NPOSS-27

Figure 2.36 $^1$H NMR Spectra of VPOSS-3NPOSS-27
Figure 2.37 $^{13}$C NMR Spectra of VPOSS-3NPOSS-27

Figure 2.38 MALDI-TOF Mass Spectra of VPOSS-3NPOSS-27
2.3.24 Synthesis of VPOSS-6BPOSS-25

The VPOSS-diyne (29.58 mg, 0.03 mmol), N₃-3BPOSS-S (200 mg, 0.07 mmol), CuBr (5mg, 0.04 mmol) were totally dissolved by dry THF into 100 mL Schlenk flask and degassed for three times. Then PMDETA (15mg, 0.09 mmol) was added. The system was degassed again and stirred for 12 h. After the reaction was completed, the solution was added into silica gel column. THF was applied to elute off the crude product. After solvent removal, silica gel column chromatography using DCM/EA= 30:1 as the eluent was applied to purify the residue and acquire the product as a white powder (196 mg, 95%).

![Chemical Structure of VPOSS-6BPOSS-25](image)

Figure 2.39 Chemical Structure of VPOSS-6BPOSS-25
Figure 2.40 $^1$H NMR Spectra of VPOSS-6BPOSS-25

Figure 2.41 $^{13}$C NMR Spectra of VPOSS-6BPOSS-25
2.3.25 Synthesis of VPOSS-6BPOSS-30

The VPOSS-diyne (25.17 mg, 0.026 mmol), N$_3$-3BPOSS-L (200 mg, 0.06 mmol), CuBr (5 mg, 0.04 mmol) were totally dissolved by dry THF into 100 mL Schlenk flask and degassed for three times. Then PMDETA (15 mg, 0.09 mmol) was added. The system was degassed again and stirred for 12 h. After the reaction was completed, the solution was added into silica gel column. THF was applied to elute off the crude product. After solvent removal, silica gel column chromatography using DCA=10:1 as the eluent was applied to purify the residue and acquire the product as a white powder (178 mg, 95%).
Figure 2.43 Chemical Structure of VPOSS-6BPOSS-30

Figure 2.44 $^1$H NMR Spectra of VPOSS-6BPOSS-30
Figure 2.45 $^{13}$C NMR Spectra of VPOSS-6BPOSS-30

Figure 2.46 MALDI-TOF Mass Spectra of VPOSS-6BPOSS-30
2.4 The Introduce of Multi Functional Groups to VPOSS Cage by Thiol-ene “Click” reaction

Up to now, a serial of VPOSS-nBPOSS (NPOSS) giant molecules with identical topological structures but different chain length has been presented. And these precisely defined ABn type giant molecules could further modified with different functional gorups by thiol-ene “click” reaction to afford a set of giant molecules occupying Janus feature. Thiol-ene “Click” Chemistry was a well-established tool for site specific functionalization. As previous work in our group, multi functional groups such as -OH, -diOH and -COOH group could be introduced into the VPOSS cage to get HPOSS, DPOSS and APOSS. The completely reacted of vinyl groups could be monitored by the disappearance of -CH=CH₂ m peaks at δ 6.15-5.71 ppm in ¹H NMR spectrum.

Figure 2.47 ¹H NMR Spectra of DPOSS-6BPOSS-30 (-CH=CH₂ m peaks at δ 6.15-5.71 ppm was completely disappeared.
CHAPTER III

SELF-ASSEMBLY BEHAVIORS OF DPOSS-nBPOSS (NPOSS) WIME SIMILAR
TOPOLOGICAL STRUCTURES BUT DIFFERENT CHAIN LENGTH

3.1 SAXS Experiments

SAXS experiments was conducted out with a Rigaku™ MicroMax 002+
instrument, equipped with a two dimensional (2D) multiwire area detector and a
microfocus sealed copper tube. The working current and working voltage were 0.6 mA and
50 KV. The wavelength of X-Ray is 0.154 nm. The scattering vector was calibrated by
standard silver behenate. The recording time for each sample was 1200 second. The data
was analyzed via SAXS gui software.

3.2 Comparison of Self-assembly Behaviors of DPOSS-2BPOSS-20 and DPOSS-2BPOSS-28

DPOSS-2BPOSS-20 and DPOSS-2BPOSS-28 samples were annealed at 165 °C for
5h, then quenched to rt via 30 °C/min. After that, SAXS experiments were conducted to
analyze the self-assembly behaviors of DPOSS-2BPOSS-20 and DPOSS-2BPOSS-28
samples. SAXS data showed that DPOSS-2BPOSS-20 could self-assemble into HEX
structure. However, when the linkers between DPOSS and BPOSS were changed from 20
atoms to 28 atoms, DPOSS-2BPOSS-28 could self-assemble into DG structure.
3.3 Comparison of Self-assembly Behaviors of DPOSS-3BPOSS-21 and DPOSS-3BPOSS-27

DPOSS-3BPOSS-21 and DPOSS-3BPOSS-27 samples were annealed at 165 °C for 5h, then quenched to rt via 30 °C/min. After that, SAXS experiments were conducted to analyze the self-assembly behaviors of DPOSS-3BPOSS-21 and DPOSS-3BPOSS-27.
samples. SAXS data showed that DPOSS-3BPOSS-21 could self-assemble into A15 Phase. However, when the linkers between DPOSS and BPOSS were changed from 21 atoms to 27 atoms, DPOSS-3BPOSS-27 could self-assemble into HEX structure.

Figure 3.3 SAXS powder patterns of DPOSS-3BPOSS-21

Figure 3.4 SAXS powder patterns of DPOSS-3BPOSS-27
3.4 Comparison of Self-assembly Behaviors of DPOSS-3NPOSS-19 and DPOSS-3NPOSS-27

DPOSS-3NPOSS-19 and DPOSS-3NPOSS-27 samples were annealed at 110 °C for 5h, then quenched to rt via 20 °C/min. After that, SAXS experiments were conducted to analyze the self-assembly behaviors of DPOSS-3NPOSS-19 and DPOSS-3NPOSS-27 samples. SAXS data showed that DPOSS-3NPOSS-19 could self-assemble into A15 Phase. However, when the linkers between DPOSS and NPOSS were changed from 19 atoms to 27 atoms, DPOSS-3NPOSS-27 could self-assemble into HEX structure.

Figure 3.5 SAXS powder patterns of DPOSS-3NPOSS-19
3.5 Comparison of Self-assembly Behaviors of DPOSS-6BPOSS-25 and DPOSS-6BPOSS-30

DPOSS-6BPOSS-25 and DPOSS-6BPOSS-30 samples were annealed at 165 °C for 5h, then quenched to rt via 20 °C/min. After that, SAXS experiments were conducted to analyze the self-assembly behaviors of DPOSS-6BPOSS-25 and DPOSS-6BPOSS-30 samples. SAXS data showed that DPOSS-6BPOSS-25 couldn’t self-assemble into any supramolecular structures. However, when the linkers between DPOSS and BPOSS were changed from 25 atoms to 30 atoms, DPOSS-6BPOSS-30 could self-assemble into A15 phase.
Figure 3.7 SAXS powder patterns of DPOSS-6BPOSS-30
CHAPTER IV
SUMMARY

In summary, a novel series of AB\textsubscript{n} type giant shape amphiphiles with similar topological structures but different chain length were successfully synthesized, proved by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra and MALDI-TOF MS experiments. The study of their self-assembly behaviors showed several obvious changes in supramolecular structure formation (such as from amorphous to A15 phase, A15 phase to HEX, HEX to DG etc.) with the change of chain length. This work would open a new insight into supramolecular structure formation of AB\textsubscript{n} type soft materials and offer a great opportunity to further understand the Frank- Kasper phases in giant molecules field.


